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SUMMARY

This work presents the results of the X-Ray Photoelectron Spectroscopy (XPS) analysis of AISI 440C ball surfaces lubricated with perfluoropolyether (PFPE) oils after friction experiments under sliding conditions at high load in air and vacuum environments. The PFPE lubricants tested were Demnum S100, Fomblin Z-25 and Krytox 143AB. It was found that all the PFPE lubricants were degraded by sliding contact causing the formation of inorganic fluorides on the metallic surfaces and a layer of organic decomposition products.

KRYTOX 143AB was the least reactive of the three lubricants tested. It was also found that metal fluoride formed at off-scar areas. This suggests the formation of reactive species, such as COF_2 or R_fCOF, during sliding experiments, which can diffuse through the lubricant film and react with the metallic surfaces away from the contact region.

Comparison of reference specimens before sliding with those that had undergone the sliding tests showed that the amount of non-degraded PFPE remaining on the surface of the balls after the sliding experiments was greater than that of the balls without sliding.

INTRODUCTION

Perfluoropolyethers (PFPE's) have been used successfully for many years to lubricate a variety of components (i.e., actuators, imaging and sounding devices, filter wheels, etc.) for space applications (Ref. 1 to 3). In the past, life limiting factors were often related to non-tribological components such as batteries and electronics (Ref. 4). Today, with the increasing demands being placed on spacecraft components (longer duration

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missions and higher reliability) the tribological systems are becoming the "weak links" (Ref. 5).

Although, PFPE's have high intrinsic thermal stability (Ref. 6), they do decompose in contact with Lewis acids (Ref. 7 to 9), various metals and metal oxides (Ref. 10 to 12) and in tribological contacts (Ref. 1, 13, and 14).

One accelerated test method to study friction and wear characteristics, as well as surface reactions, involves the use of a vacuum four ball apparatus (Ref. 15). Recently, the tribological characteristics of three commercially available PFPE lubricants (Krytox 143AB, Demnum S100, and Fomblin Z-25) were reported (Ref. 16).

The objective of this paper is to report the results of an x-ray photoelectron spectroscopy analysis of the worn 440C steel surfaces from the experiments reported in Reference 16. This information will provide insight in elucidating the mechanism of boundary lubrication for PFPE lubricants. In addition, it will provide a baseline for comparison with future studies of lubricant additives.

EXPERIMENTAL

Vacuum Tribometer

The vacuum tribometer used in these experiments is shown in **Figure 1.** The test specimen configuration of the tribometer is shown in **Figure 2.** In the vacuum tribometer, AISI 440C stainless steel precision bearing balls, 9.525 mm (3/8") in diameter, are used as test specimens. Description of the tribometer is reported in detail elsewhere (Ref. 15).

The rotating top ball of the tribometer is mounted on a ferro-fluidic vacuum rotary feedthrough. The lower three stationary balls are mounted in a ball holder which also acts as the lubricant reservoir. This ball holder is mounted on the top of a flex-pivot whose bottom part is fixed to a linear motion feedthrough (bellows sealed) manipulator which can be raised or lowered from outside the chamber with a pneumatic cylinder. Friction torque is recorded by measuring the angular displacement of the ball holder-lubricant cup mounted on the top (movable) of the flex-pivot versus the bottom of the flex-pivot (fixed) by a set of Hall-effect position sensors. In this study, the tests are carried out at constant sliding speed, $2.88 \cdot 10^{-2}$ m/s (100 rpm), and an axial load of 600 N. All tests are conducted at room temperature (23°C) and at a base pressure of $\approx 10^{-5}$ Pa or dry air at atmospheric pressure.

The balls used in these studies are cleaned with levigated alumina, rinsed with distilled water and methanol and stored in a vacuum desiccator before use. The lubricant reservoir, filled with the lubricant, is evacuated in a separate vacuum system in order to remove dissolved gases. After this process, the cup is quickly introduced into the tribometer. Several ball specimens are analyzed after various stages of wear testing, these three sets of sample treatments used for the balls are listed below:

Sample Designation	Treatment
1. Reference	Cleaned, unlubricated, and no wear
2. Pre-wear	Cleaned, lubricated, then soxhlet extracted in trichlorotrifluoro-ethane (TCF) but no wear.
3. Post-Wear (s)	Cleaned, lubricated, subjected to tribometer test as a stationary ball, then soxhlet extracted in TCF.
Post-Wear (r)	Same as above but tested as a rotating ball in the tribometer.

In addition, two different areas are analyzed on the post-wear balls. These are illustrated for the stationary balls in **Figure 3** (on-scar and a region 90° away from the scar, designated as off-scar). Analogous areas are analyzed for the rotating balls.

Lubricants Tested

Three kinds of commercially available PFPE lubricants are used in order to compare their tribological characteristics. These lubricants are DEMNUM S100, FOMBLIN Z-25, and KRYTOX 143AB. Some of their physical properties are listed in **Table 1.** They have similar viscosities at room temperature (the temperature at which the tests were conducted).

DEMNUM has a linear backbone where the repeating unit is $-(CF_2CF_2CF_2O)n-$. FOMBLIN Z also has linear structure where the perfluorinated ethylene oxide group, $-(CF_2CF_2O)-$, and the difluoroformyl group, $-(CF_2O)-$, combine randomly in a ratio 0.6 to 0.7. In KRYTOX, the repeating unit is $-(CF(CF_3)CF_2O)n-$, where the $-CF_3$ is a pendant group.

X-ray Photoelectron Spectroscopy

The analyses of the balls were performed with a (VG) Mk II ESCALAB XPS system described elsewhere (Ref. 12). The major difference in the present study is that a monochromatic Al Kα x-ray source was used, in order to minimize damage to the PFPE film (Ref. 17). The diameter of the circular area of analysis was 1 mm. The regions analyzed were F 1s, Fe $2p_{3/2}$, O 1s and C 1s. The total acquisition time was 72 min. A previous assessment (Ref. 12) of fluid degradation caused by the x-ray irradiation indicated that no damage was detected as a result of exposure time. The balls were removed from the test rig, and then cleaned to eliminate excess fluid remaining on the surface. The cleaning was done by Soxhlet extraction with hot 1,1,2 -trifluorotrifluoroethane (TCF) solvent for ~ 72 hrs. After this procedure, only a thin film (<50Å) of lubricant remained on the surface, allowing XPS analysis of the metal/lubricant interface.

The balls were mounted on a modified VG stub and fixed with "dag", a conductive graphite powder suspended in an isopropanol solution. After the wear scar was analyzed, the holder was rotated 90° and the off-scar region was analyzed. XPS spectra were taken from the wear scar of the stationary ball, a wear track on the rotating ball and the off-scar areas of both

stationary and rotating balls. The spectra were all taken at normal exit, **Figure 3.** All balls analyzed are listed in **Table 2.** The 'r' in the ball identification stands for 'rotating' which, in general, gave more intense signals due to larger worn areas and 's' stands for 'stationary'.

As a background comparison, a cleaned unlubricated (reference) ball and balls (pre-wear) covered with the three PFPE fluids, and then subjected to the solvent extraction process described above were analyzed. None of these balls had been used previously in the tribometer.

RESULTS

Figures 4, 5, and 6 contain XPS spectra for runs in vacuum for Fomblin Z, Demnum, and Krytox, respectively. Each figure contains four high resolution spectral regions (F 1s, O 1s, C 1s, and Fe 2p3/2). Spectra for four different ball specimens appear in each region. These are: (a) post-wear(s), stationary, on-scar; (b) post-wear(s), stationary, off-scar; (c) pre-wear; and (d) reference. The rotating ball scar was analyzed and the results are included, but no spectra is shown in this report

On-Scar Area

The analytical results of the on-scar regions for balls run under vacuum conditions for Fomblin Z, Demnum, and Krytox appear as curves a in Figures 4a, 5a, and 6a, respectively. The F 1s spectra show the presence of metallic fluoride at 685.0 eV and C-F bond at 688.7 eV, for all three lubricants. The O 1s spectra show the presence of oxide (530.2 eV), hydroxide (531.5 eV), C-O-F containing compounds (532.0 and 533.4 eV) and the non-degraded lubricant at 535.5 eV. For all lubricants, the oxide peak is the predominant feature in the O 1s region.

The C 1s spectra of the three fluids are similar. All show a surface contaminant peak at 285.2 eV, some C-O-H, and C-O-F containing compounds in the 286-289 eV region, the CF_2 peak at 291.5 eV, and C-F bond at higher binding energy (293.5 eV), that can be atributed to non-degraded lubricant. The Fe $2p_{3/2}$ spectra show the metallic iron peak at 706.7 eV, and a broader peak at 709.8 eV that can be assigned to the presence of oxide, hydroxide, and fluoride in the overlayer. The higher intensity of the Fe $2p_{3/2}$ signal indicates that the thickness of the overlayer decreased when compared with lubricated, extracted, pre-wear balls (spectra c).

Off-Scar Area

The spectra for the off-scar regions, an area 90° from the scar, are shown in Figures 4b, 5b, and 6b. The results for each spectral region are similar to the corresponding regions recorded in the on-scar area. The F 1s signal shows metallic fluoride and C-F containing species, which can be related to non-degraded lubricant, when matched with the C 1s and O 1s signal, although with less intensity than the on-scar region, indicating that both amounts are smaller. The O 1s signal shows the presence of

similar compounds as detected in the on-scar region, but the relative intensities have changed. In general, the O 1s signal is greater due to the larger oxide-hydroxide intensities. The signal from the lubricant has decreased, compared to the on-scar area (similar to the result from the F 1s spectrum). The relative intensities of the oxide-hydroxide region has also changed, showing an increase in the oxide signal.

The C 1s regions show again a smaller signal from the lubricant than the on-scar area, in agreement with the F 1s and O 1s spectra. A more detailed study (curve fitting) of the C 1s spectra indicates that there is lubricant that is intact and has not undergone any decomposition, unfortunately this is not very clear in the figures. Nevertheless, other peaks related to carbon-oxygen containing compounds are present in this region. These compounds are also present in those spectra from the on-scar area. No compounds formed by C, O, and F, previously related to decomposition products of the PFPE (Reference 12), are found in this region. A comparison of the C 1s curve fitting for both areas, on and off the scar, show that there is much less 291.5 peak in Figure 4b, indicating the absence of the $-CF_2-$ species, a product of Fomblin Z degradation. This species is found in the on-scar area (**Figure 4a**).

In summary, the overlayer for the on-scar area is composed of oxide, hydroxide, metallic fluoride, C-O-H and C-O-F containing compounds from PFPE degradation, and non-degraded PFPE excess fluid remaining on the surface. The off-scar area has a thinner film, composed of oxides, hydroxides, metallic fluorides, C-O-H containing compounds and non-degraded lubricant.

Lubricated-Extracted Balls (Pre-Wear)

Figures 4c, **5c**, and **6c** show the XPS spectra of clean pre-wear balls lubricated with Fomblin Z, Demnum and Krytox, respectively, then subjected to solvent cleaning by soxhlet extraction. The same cleaning procedure was used for the post-wear balls from the tribometer. The amount of fluid remaining on the surface of the pre-wear, lubricated ball is much less than that of the post-wear balls. The XPS spectrum, for each of the three lubricants, from the pre-wear balls, shows no C 1s signal in the 293-296 eV region that corresponds to the carbon signal from the PFPE's. The presence of PFPE is detected only by the small F 1s peak (688.7 eV). No O 1s peak in the 534-536 eV region corresponding to the PFPE is detected. In contrast, appreciable amounts of non-degraded PFPE, and other organic compounds containing C, O and possible F are detected in the spectra of the balls that had been exposed to the tribological environment, even in off-scar areas.

Clean Unlubricated Balls (Reference)

Figure 4d shows the XPS spectra of a clean unlubricated, reference ball. These same spectra are reproduced in Figures 5d and 6d. The XPS analysis of the Fe $2p_{3/2}$ and O 1s shows the presence of an inorganic layer formed by both oxides and hydroxides, from exposure to atmosphere. The hydroxide is the

largest peak in the O 1s region. The C 1s region shows the usual adventitious carbon contaminant peak (284.7-285 eV). Also a small peak at 288.7 eV is detected which could be related to the presence of -C-O- containing contaminants. No metallic carbide peak is visible (283.3 eV). In the Fe $2p_{3/2}$ region, the Fe° metallic peak at 707.2 eV is still visible, together with the oxidized Fe^{+x} peaks. The attenuation of the metallic Fe° peak indicates that the oxide and hydroxide layer formed is about 4-5 nm thick, as expected for 440C samples that had been exposed to atmosphere.

DISCUSSION

Organic and inorganic compounds on the surface of the post-wear balls have been clearly identified. The organic component of this surface layer can be attributed to the degradation products of PFPE, and to non-degraded lubricant. Due to the complexity of the system, all XPS peaks in the C 1s and O 1s regions, related to the decomposition products of PFPE, have not been assigned. The inorganic component of the surface layer is formed by the original oxide and hydroxide mixture resulting from atmospheric exposure, plus a newly formed metal fluoride. The metal fluoride is easily identified in the F 1s XPS spectra at 684-686 eV.

By comparing the XPS results for the post-wear balls with pre-wear balls it can be seen that post wear balls, on scar showed more C-F containing compounds than off the scar region or the pre-wear balls indicates that exposure to the tribo-environment induces PFPE degradation and a greater ability for non-degraded PFPE to adhere to the surface.

CARBON RATIO

An attempt is made to determine the amount of non-degraded lubricant remaining on the surface by taking the ratio of the area under the XPS curve of the C 1s peak from the non-degraded PFPE (B.E.≈293.3 eV), C_{PFPE}, against the area of the adventitious carbon peak (B.E.=284.7 eV), C_C. This expression is called the Carbon Ratio. The results are shown in **Table 3** in the column labelled carbon ratio for stationary and rotating, on and off-scar, and for runs in air and vacuum. Krytox always shows a Carbon Ratio of less than 1.0 which is, in general, smaller than the ratios for Fomblin Z and Demnum. The amount of lubricant remaining on the surface after extraction depends on both its surface affinity and on its solubility in the extraction solvent (TCF). Independent of solvent solubility is the observation that exposure to the tribo-environment increases the ability of the lubricant to adhere to the surface.

Formation of Metal Fluoride

The F 1s spectra (a and b) in Figures 4 to 6 show the presence of residual, non-degraded PFPE and the formation of metallic fluoride both on-scar and off-scar. From the data in the F 1s region, the peak area ratios of PFPE and metal fluoride

($F_{flouride}/F_{PFPE}$) are shown in **Table 3.** It should be noted that no metallic fluoride forms just by lubricating the ball with PFPE without any tribo-contact (pre-wear), as seen in Figures 4c, 5c, and 6c. Therefore, it can be concluded that a reaction between the PFPE and the metal surface is induced only by tribo-contact. In addition, metallic fluoride is also detected on the off-scar area. This suggests, that during the tribo-experiment, the formation of reactive mobile species, such as COF_2 or R_fCOF, can diffuse through the lubricant film and react with metal surfaces without any direct mechanical sliding.

As mentioned above, the amount of non-degraded PFPE remaining on the surface is different for each lubricant. Therefore, the absolute amount of metallic fluoride formed on the surface can not be measured simply by the attenuation of the substrate peaks, since this value is distorted due to the presence of the PFPE overlayer.

FLUORINE RATIO

In an attempt to quantify the amount of metallic fluoride on the surface, a new expression, Fluorine Ratio, is defined. The Fluorine Ratio is the ratio of the F 1s signals. Namely, the peak area of the F 1s signal for the metallic fluoride, divided by the signal of the PFPE. These values are tabulated in **Table 3.** This ratio is considered to be a better estimate of the amount of fluoride present on the surface than the fluoride F 1s peak alone (B.E.=684.5 eV). Also, in Table 3, a similar ratio for carbon is tabulated in the column, Carbon Ratio. The Carbon Ratio, as mentioned before, is a measure of the amount of lubricant remaining on the surface after extraction. Both, Fluorine and Carbon Ratio's should be examined when quantifying the metallic fluoride present on the surface. Thus, Demnum shows large values for Carbon Ratio, indicating the balls lubricated with this fluid retained more lubricant than those lubricated with Fomblin Z or Krytox. With Demnum we should observe, therefore, the smallest values for the Fluorine Ratio, since the fluoride formed is buried under several layers of lubricant. The data show this is the case for on and off scar samples.

AIR ENVIRONMENT

It can also be seen, in general, that the balls run in air retained more lubricant than the balls run in vacuum for similar Fluorine Ratios. Other information that can be extracted from **Table 3** is that the amount of lubricant retained on the surface after extraction is independent of the amount of metallic fluoride formed on the surface. It is definitely related to the characteristics of the lubricant itself.

VACUUM ENVIRONMENT

In **Figure 7** and **Table 4** the Fluorine Ratio is shown as a function of the wear scar diameter for the stationary balls (Figure 7a) and rotating ball (Figure 7b) run under vacuum conditions. For plotting purposes, it is assumed that the wear

scar of the rotating ball is the same size as the stationary ball. It can be seen that the stationary and rotating ball show opposite behavior. For the stationary ball, the wear scar diameter and amount of fluoride formation increase in the following order:Krytox<Demnum<Fomblin Z. This trend is reversed for the rotating ball in vacuum. Similar phenomenon, referred to as wear asymmetry, has been observed by Willermet and Kandah (Ref. 18). No trend is observed for the balls run in air, as shown in **Table 5** and Figures 7c and 7d.

Summary of Results

1. Metal fluoride is detected both on and off wear scar areas, but not on pre-wear (clean, lubricated, extracted) balls which were not exposed to the tribo-environment.
2. More PFPE lubricant is retained on the surface when a degraded PFPE layer is present.
3. The larger the wear scar on the stationary balls run in vacuum, the greater the amount of fluoride forms in and off the wear scar areas. The reverse is true for the rotating balls.
4. For stationary balls run in vacuum, the amount of fluoride formed and the wear scar size are the greatest for balls lubricated with Fomblin Z.

CONCLUSIONS

1. Unformulated PFPE lubricants under boundary lubrication conditions operate in the corrosive wear regime. This is caused by the production of reactive fluorinated species which form fluorides in contact with surface oxides.
2. The presence of surface fluoride enhances the adsorption of unreacted PFPE lubricants thus making it more difficult to remove by solvent extraction.
3. The decomposition products formed in the wear scar areas with Fomblin Z are chemically similar to those produced solely by thermal means, previously reported (Reference 12).

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Table 1. Physical Properties of Sample Oils

Oil Name		FOMBLIN Z-25	DEMNUM S100	KRYTOX 143AB
Molecular Weight		15000	5600	3700
Viscosity, mm^2/s	@ 20°C	255	250	230
	@ 40°C	135	96.0	75
	@ 100°C	30.0	18.2	9.7
Viscosity Index		360	209	113
Density, g/cm_3		1.851	1.878	1.894
Pour Point, °C		-66	-60	-40

Table 2. List of Balls Analyzed

Key	Ball	Environment	Analysis Area	Test Fluid
K1r	Rotating	Vacuum	On-Scar	KRYTOX 143AB
K1r′			Off-Scar	
K2s	Stationary		On-Scar	
K2s′			Off-Scar	
K7r	Rotating	Air	On-Scar	
K7r′			Off-Scar	
K8s	Stationary		On-Scar	
K8s′			Off-Scar	
F3r	Rotating	Vacuum	On-Scar	FOMBLIN Z-25
F3r′			Off-Scar	
F4s	Stationary		On-Scar	
F4s′			Off-Scar	
F7r	Rotating	Air	On-Scar	
F7r′			Off-Scar	
K8s	Stationary		On-Scar	
K8s′			Off-Scar	
D4r	Rotating	Vacuum	On-Scar	DEMNUM S100
D4r′			Off-Scar	
D3s	Stationary		On-Scar	
D3s′			Off-Scar	
D5r	Rotating	Air	On-Scar	
D5r′			Off-Scar	
D6s	Stationary		On-Scar	
D6s′			Off-Scar	
Reference	Clean Ball	-	-	Unlubricated

Table 3. The Amount of Residual, Non-degraded PFPE and Metal Fluoride Formed

Key	Environment	Analysis Area	Test Fluid	Carbon Ratio, C_{PFPE}/C_C	Scar Size (mm)	Fluorine Ratio, $F_{FLUORIDE}/F_{PFPE}$
F3r	Vacuum	On Scar	FOMBLIN Z	1.91	-	0.08
F4s				0.64	0.81	0.25
F4r′		Off Scar		2.40	-	0.02
F4s′				0.30	-	0.10
F7s	Air	On Scar		1.45	-	0.21
F8s				0.38	0.72	0.25
F7r′		Off Scar		2.50	-	0.15
F8s′				0.41	-	0.14
D4r	Vacuum	On Scar	DEMNUM	0.63	-	0.24
D3s				2.82	0.70	0.21
D4r′		Off Scar		0.45	-	0.09
D3s′				0.91	-	0.06
D5r	Air	On Scar		5.14	-	0.04
D6s				1.24	0.58	0.14
D5r′		Off Scar		6.64	-	0.02
D6s′				1.50	-	0.04
K1r	Vacuum	On Scar	KRYTOX	0.40	-	0.61
K2s				0.43	0.60	0.10
K1r′		Off Scar		0.51	-	0.05
K2s′				0.22	-	0.04
K7r	Air	On Scar		0.77	-	0.42
K8s				0.38	0.39	0.25
K7r′		Off Scar		0.76	-	0.16
K8s′				0.41	-	0.14

Table 4. Wear Scar Size and Fluorine Ratio for Post-Wear Balls Run in Vacuum (On-Scar)

VACUUM				
Fluid		Wear Scar Diameter (mm)	Fluorine Ratio $F_{FLUORIDE}/F_{PFPE}$	
Stationary	Rotating		ROTATING	STATIONARY
Fomblin Z (F4s)	F3r	.81	.08	.25
Demnum (D3s)	D4r	.70	.24	.21
Krytox (K2s)	K1r	.60	.61	.10

Table 5. Wear Scar Size and Fluorine Ratio for Post-Wear Balls Run in Air (On-Scar)

AIR				
Fluid		Wear Scar Diameter (mm)	Fluorine Ratio $F_{FLUORIDE}/F_{PFPE}$	
Stationary	Rotating		ROTATING	STATIONARY
Fomblin Z (F8s)	F7r	.72	.21	.25
Demnum (D6s)	D5r	.58	.04	.14
Krytox (K8s)	K7r	.39	.42	.25

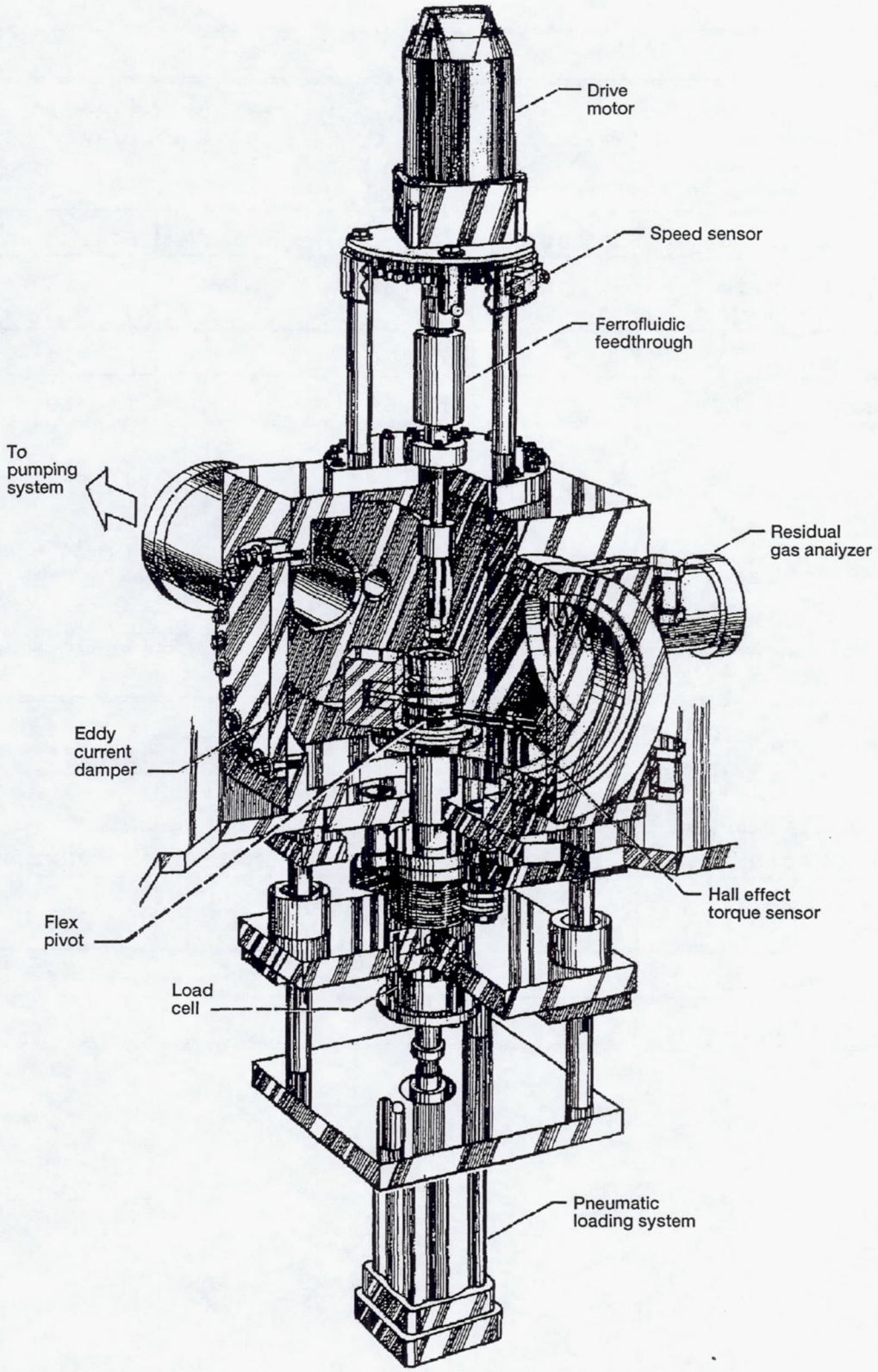

Figure 1.—Vacuum four-ball tribometer.

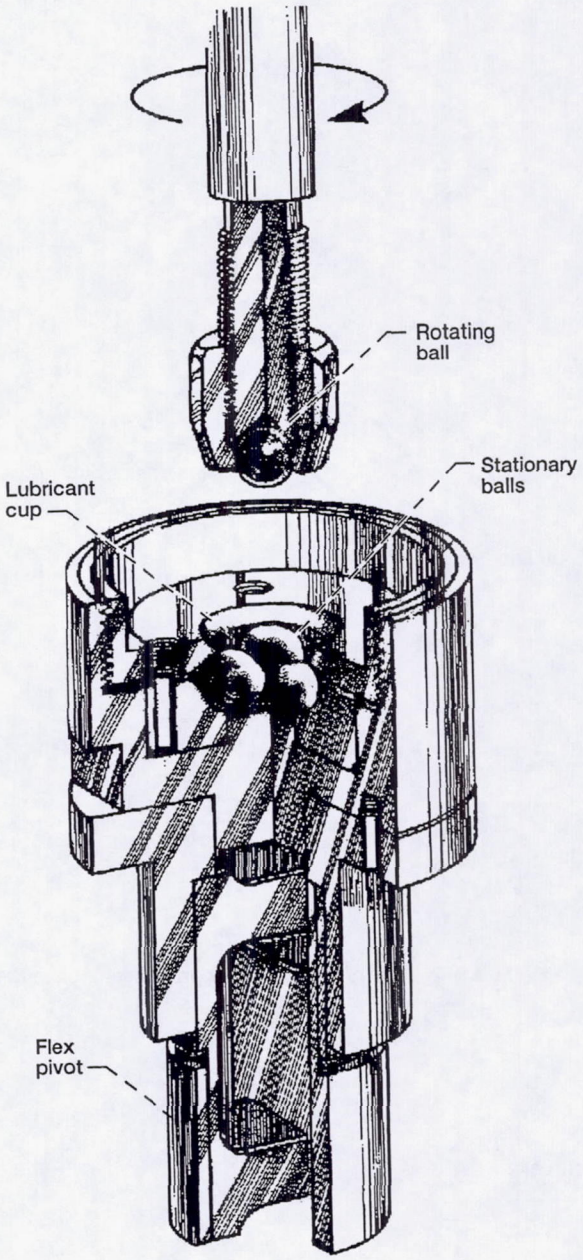

Figure 2.—Test specimen configuration.

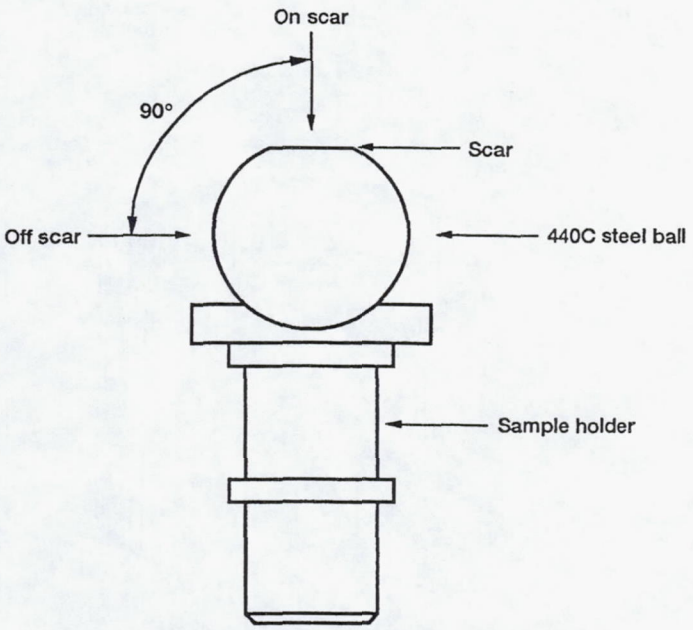

Figure 3.—Stationary ball wear scar orientation during XPS analysis.

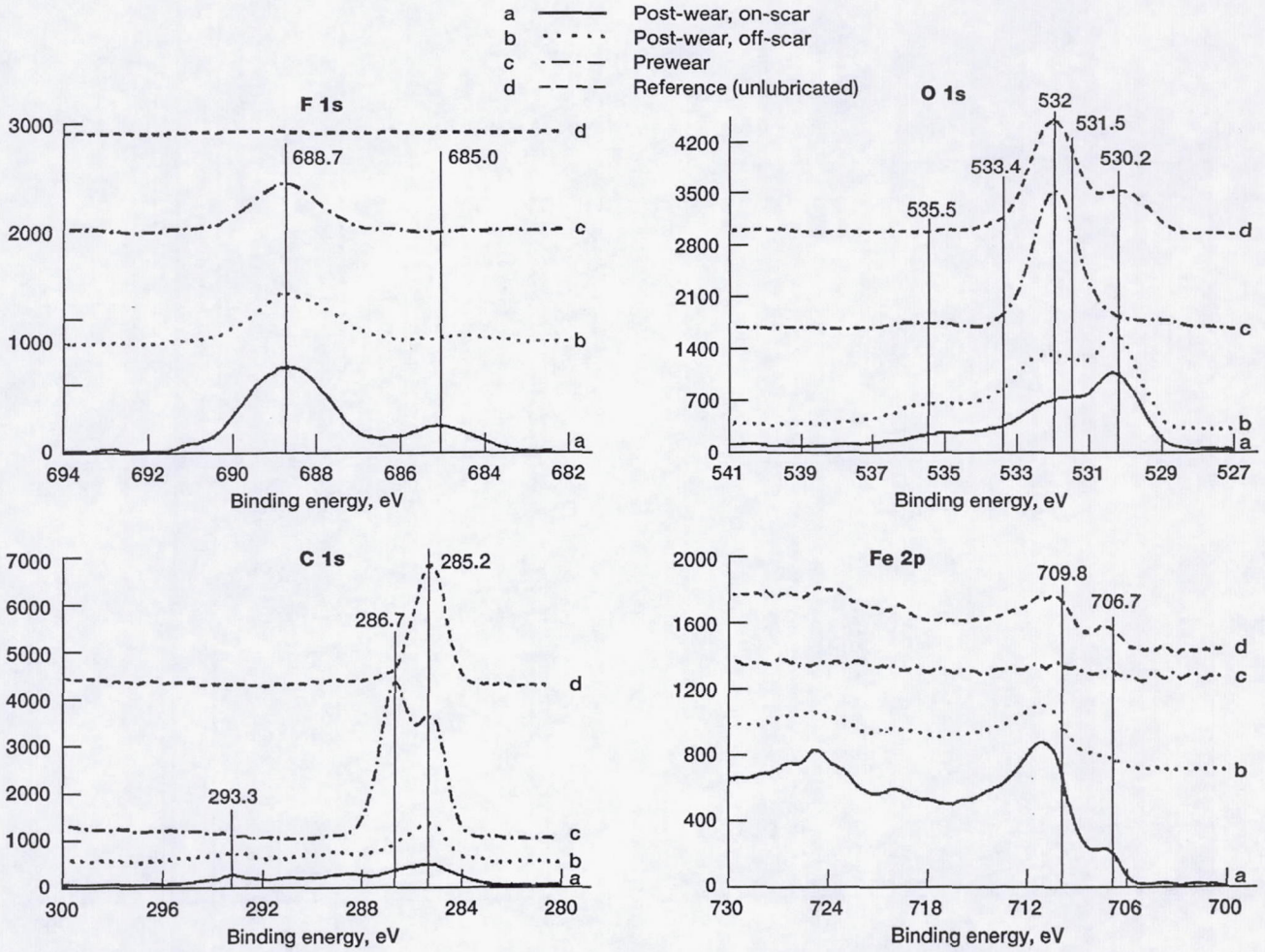

Figure 4.—High resolution XPS spectra for various regions of 440C steel specimens lubricated with Fomblin Z-25. The spectra a, b, c, and d have been offset in the y-axis for comparison.

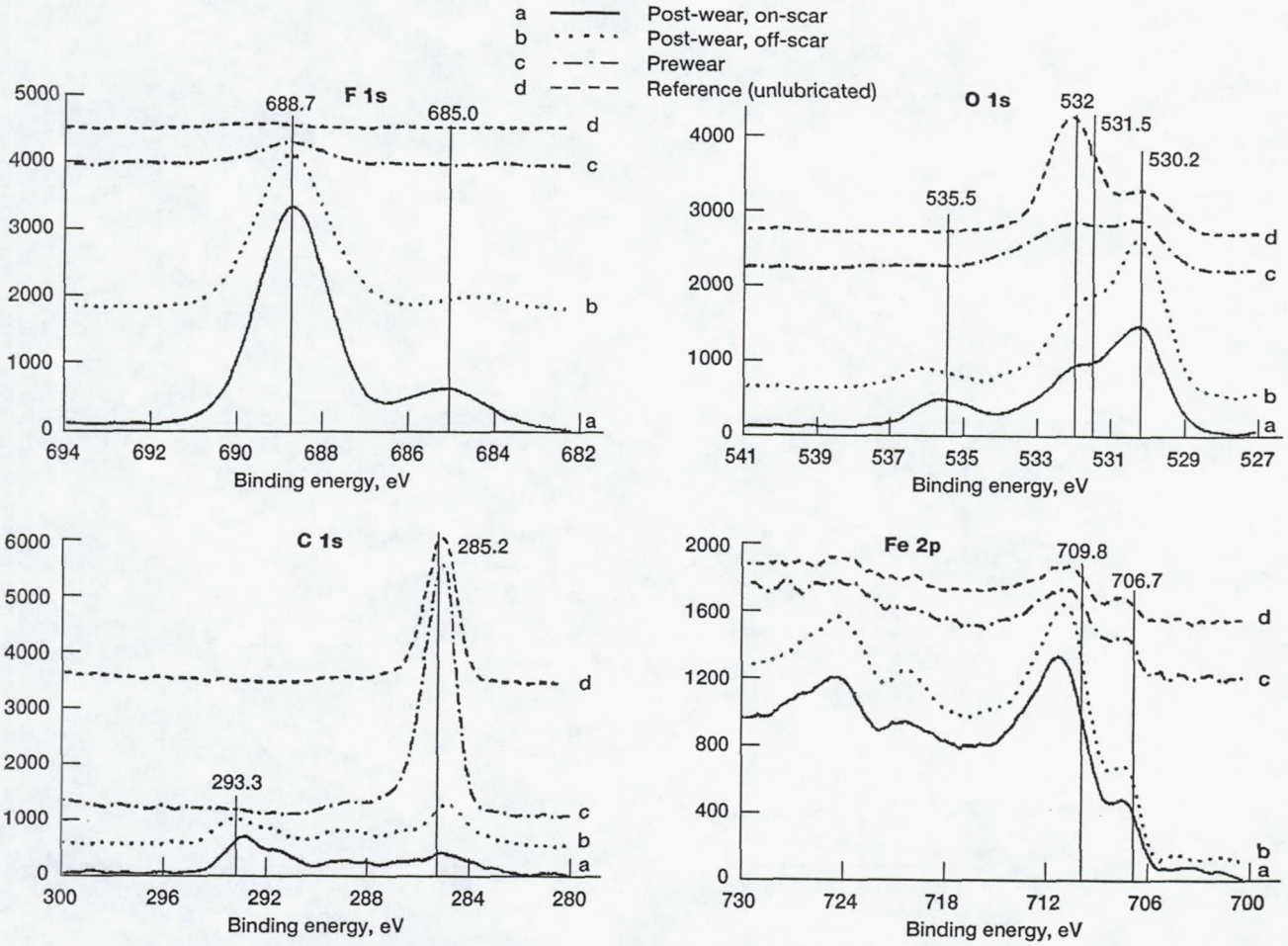

Figure 5.—High resolution XPS spectra for various regions of 440C steel specimens lubricated with Demnum S-100.

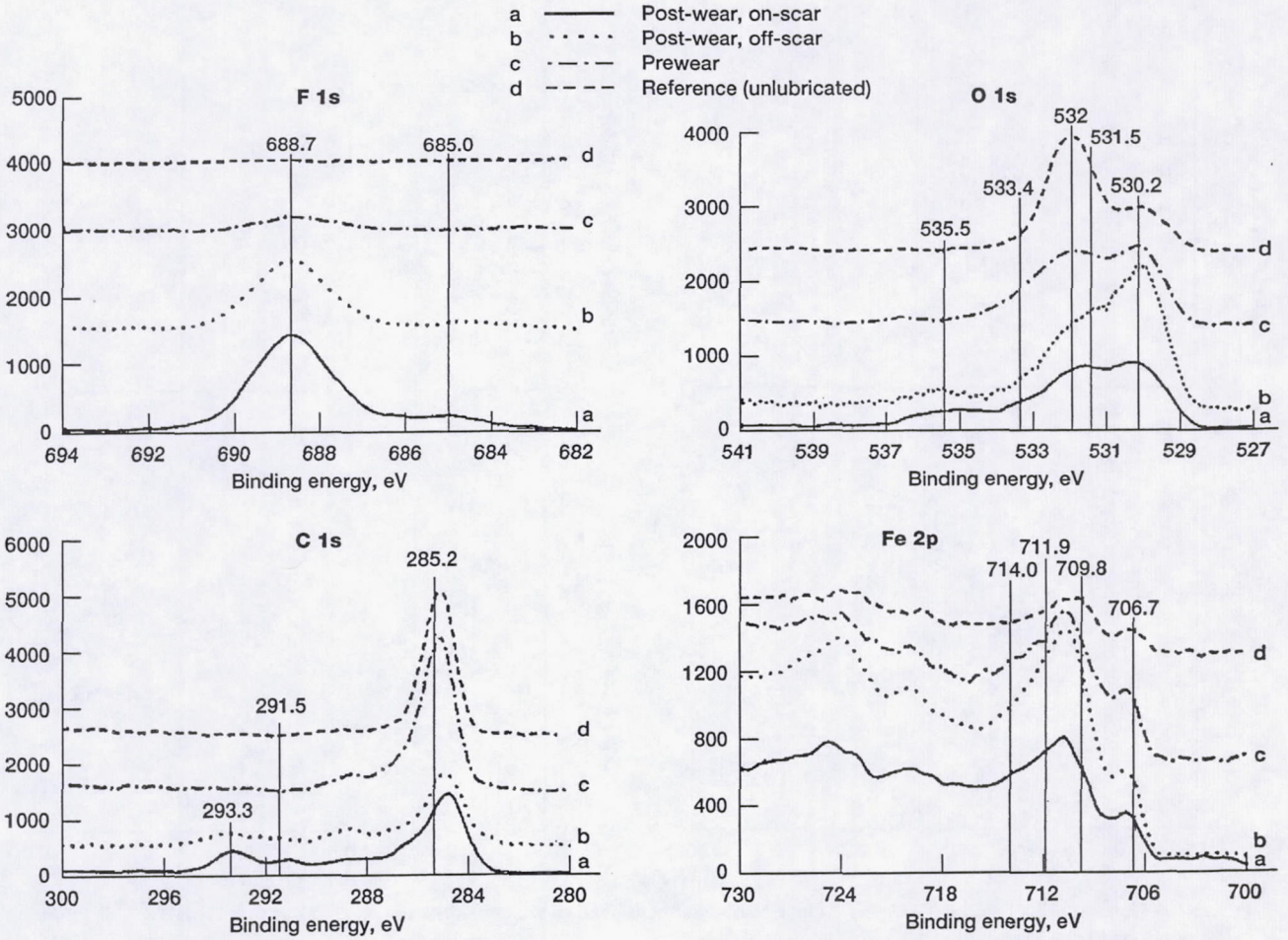

Figure 6.—High resolution XPS spectra for various regions of 440C steel specimens lubricated with Krytox 143AB.

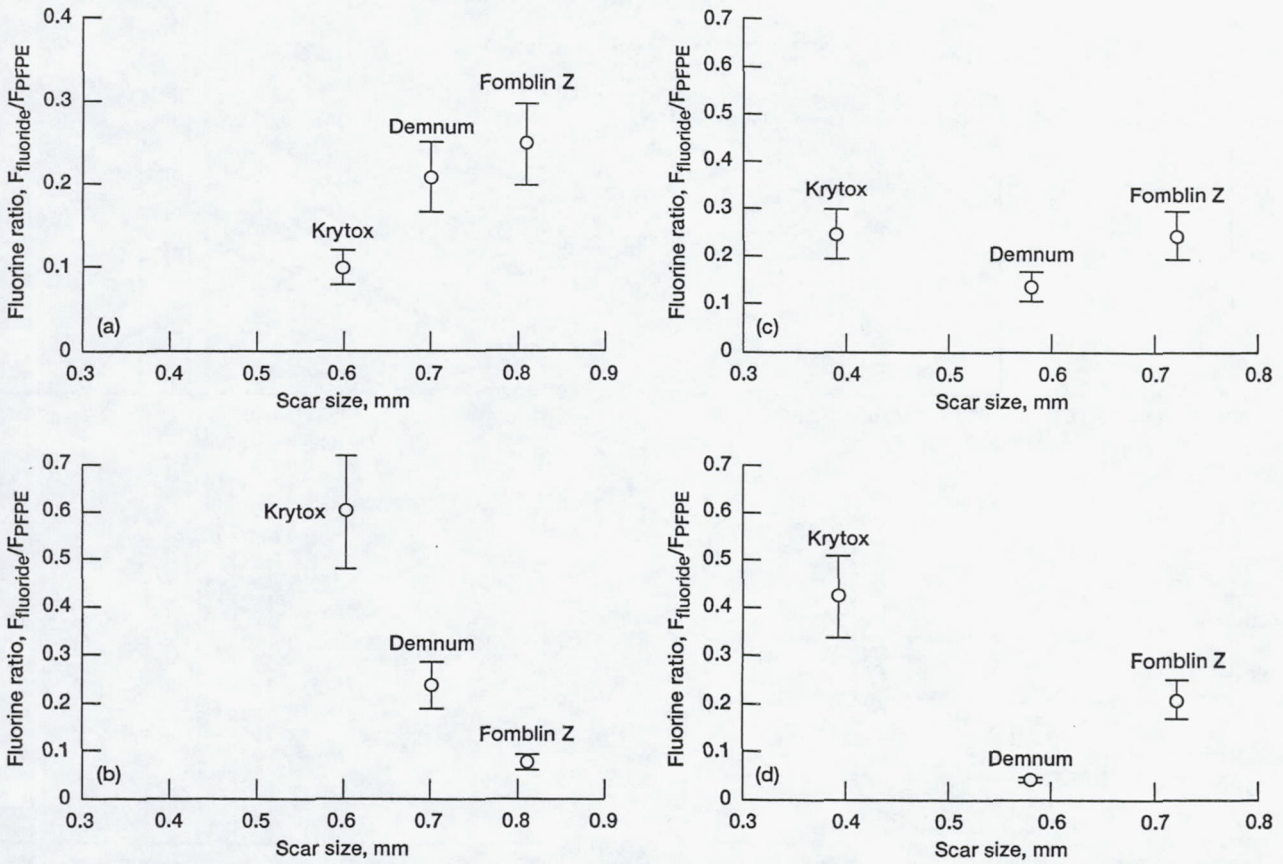

Figure 7.—Fluorine ratio, $F_{fluoride}/F_{PFPE}$ as a function of wear scar size. (a) Vacuum stationary ball. (b) Vacuum rotating ball. (c) Air stationary ball. (d) Air rotating ball.

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13. ABSTRACT ***(Maximum 200 words)***

This work presents the results of the X-Ray Photoelectron Spectroscopy (XPS) analysis of AISI 440C ball surfaces lubricated with perfluoropolyether (PFPE) oils after friction experiments under sliding conditions at high load in air and vacuum environments. The PFPE lubricants tested were Demnum S100, Fomblin Z-25 and Krytox 143AB. It was found that all the PFPE lubricants were degraded by sliding contact causing the formation of inorganic fluorides on the metallic surfaces and a layer of organic decomposition products. KRYTOX 143AB was the least reactive of the three lubricants tested. It was also found that metal fluoride formed at off-scar areas. This suggests the formation of reactive species, such as COF_2 or R_fCOF, during sliding experiments, which can diffuse through the lubricant film and react with the metallic surfaces away from the contact region. Comparison of reference specimens before sliding with those that had undergone the sliding tests showed that the amount of non-degraded PFPE remaining on the surface of the balls after the sliding experiments was greater than that of the balls without sliding.

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